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THE UNIVERSITY OF
WESTERN ONTARIO

Department of Physics
Molecular Excitation Group

Identification
Atlas of
Molecular Spectra

3. The $N_2^+ B^2\Sigma_u^+ - X^2\Sigma_g^-$
First Negative System of Nitrogen

by

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April 1965

London, Ontario

ABSTRACT

This report contains a set of vibrationally identified spectrograms of the First Negative System of Ionised Nitrogen ($N_2^+ B ^2\Sigma_u^+ - X ^2\Sigma_g^+$). A compilation of all the available molecular data on the states involved, a brief description of the appearance, occurrence and history of the system and a selected bibliography are also included.

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ACKNOWLEDGEMENTS

Research grants from the Ontario Research Foundation for the past few years have maintained the continuing "Identification Atlas of Molecular Spectra" project and made possible the production of this report.

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We would like to thank Mr. W. R. Jarmain for allowing us to use his programme for computing the Klein-Dunham potential functions of Fig. 3 and Tables IX and X. Mr. G. Drake obtained the spectra used for plates 1-4.

One of us (D. C. T.) held a National Research Council of Canada Post-Doctoral Fellowship during the tenure of which the report was prepared.

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PREFACE

During the past decade, spectroscopic methods and techniques have been increasingly employed for a variety of research purposes in many branches of physics, chemistry, aeronomy and astronomy, and a need for a working knowledge of spectroscopic methods has been felt by many whose main field of research is not spectroscopy *per se*.

Positive identification of spectroscopic features is the first and most common requirement in any application of spectroscopy to research, whatever its orientation. Wavelength lists of many atomic lines and some molecular bands are of course available and well known. Wavelength coincidence alone, however, is not always sufficient for positive identifications and photographic atlases for direct comparison with experimental spectra are always extremely useful.

Such atlases are neither common nor comprehensive. The purpose of the present series of reports is thus to provide photographs (at two or three commonly used dispersions) of important band systems, to each set of which vibrational numbering and a wavelength scale have been added for direct comparisons with experimental spectra for which identifications are sought. The reciprocal dispersions most commonly used in the reports are: high ($\sim 150 \text{ \AA/mm}$), medium ($\sim 15 \text{ \AA/mm}$) and low ($\sim 5 \text{ \AA/mm}$). In addition to the identified photographs each report includes brief comments on the character of the spectrum, its common conditions of occurrence and excitation, some historical background of the relevant research, a bibliography of papers which have been found most valuable in the compilation

of the atlas, and a tabulation of essential molecular data. Emphasis is placed on vibrational rather than on rotational structure as it is with vibrational structure of band systems that the first problems of identification usually arise in practice.

The most valuable single aid to identification of molecular spectra is of course, Pearse and Gaydon's indispensable work "The Identification of Molecular Spectra" (1941, 1950, 1963). The tables in this are arranged with the practical spectroscopist in mind, and the photographic reproductions of a number of common and important molecular spectra are particularly useful. The comparable work "Données Spectroscopiques" edited by Rosen (1951) presents the wavelengths of many band systems in Deslandres tables, essential molecular constants and a very complete bibliography (up to 1950). Two significant compilations of molecular spectra which are important in astronomical and aeronomical applications have recently been published by Wallace (1962a, b). He has the user very much in mind and gives very useful bibliographies.

Phillips and his colleagues at Berkeley (1963) are making distinguished contributions to the detailed compilation of rotational structure (to high quantum numbers) of band systems important in astronomy. Bass and Broida (1953, 1961) have produced valuable spectrophotometric atlases of OH and CH in which the rotational structure is clearly identified. Dieke and his colleagues (1959, 1962) have done a similar service to N₂ and OH band systems. Herman and Hornbeck (1951) published an

article some years ago in which vibrational identifications were made of many of the spectra commonly met in combustion spectroscopy.

The important "Molecular Spectra of Metallic Oxides" produced by Fr. Junkes and his colleagues at the Vatican Observatory is a most useful identification aid for metallic oxide spectra, especially those of astrophysical interest.

While the present series of reports is not as ambitious as some of the above works, it is hoped that it will fill a gap which many have felt existed in the reference literature of molecular spectroscopy.

R. W. NICHOLLS, *Editor*

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$N_2^+ B^2\Sigma_u^+-X^2\Sigma_g^+$ FIRST NEGATIVE SYSTEM

1. INTRODUCTION

Nitrogen is a major constituent of the atmosphere. Its spectrum is easily excited and it is an important contributor to the spectrum of all luminescent atmospheric phenomena. Therefore N_2 and its spectrum have been studied in much detail for many years.

The First Negative System of N_2^+ lies in the spectral region 2900A-5900A and some 125 bands of the system have been reported to date. The main bands of the system are readily excited, occurring in the negative glow of almost any discharge through air or nitrogen. They are blue degraded and the three most prominent sequences occur in the wavelength regions 3550A ($\Delta\nu = 1$), 3900A ($\Delta\nu = 0$) and 4250A ($\Delta\nu = -1$). The relative intensities of these sequences are usually (very roughly) 1:2:1.

The transition which gives rise to the system is $B^2\Sigma_u^+-X^2\Sigma_g^+$. The position of these levels with respect to other levels of N_2^+ is shown in Fig. 1, together with other known transitions of N_2^+ .

The constants of the states involved and a Deslandres table of observed band heads are given in Tables I and II respectively.

The most commonly observed bands lie in the $-2 < \Delta\nu < 2$, $v' < 5$, sequences and all these bands are blue degraded. However under favourable circumstances many more bands, some red degraded, are excited, most being tail bands of these sequences.

2. SPECTRAL FEATURES

The system has been observed over a wide range of vibrational energy levels; the highest

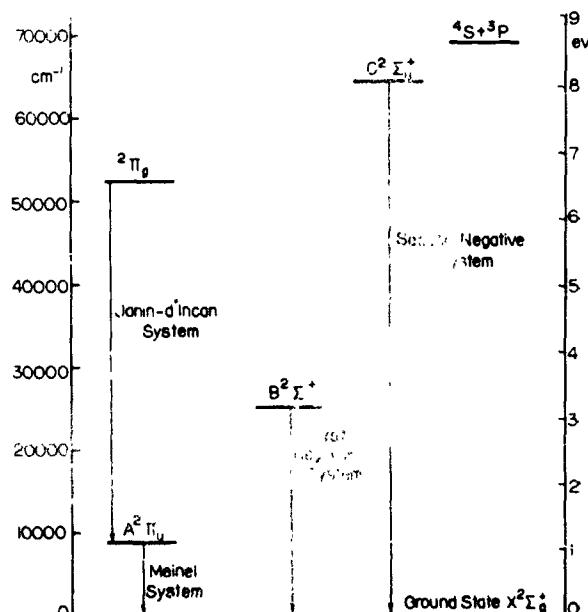


Fig. 1. Observed levels and systems of N_2^+

values so far observed are $v = 29$ for the $B^2\Sigma_u^+$ state and $v = 23$ for the $X^2\Sigma_g^+$ state. All observed bands with $v' < 7$ and also those with $8 < v' < 11$ and $\Delta\nu < -1$, are blue degraded. All observed bands with $v' > 12$ and those with $v' = 10, 11$, $\Delta\nu > 0$ are red degraded (Fig. 2) although some appear headless on weak exposures. These are the so-called tail bands of the system. Very few bands have been observed in the region $6 < v' < 9$, $\Delta\nu > 0$; it can be predicted however that in the main these bands will be weakly degraded and overlapped by other stronger bands of the system (Tyte 1962).

The rotational structure of the system is very

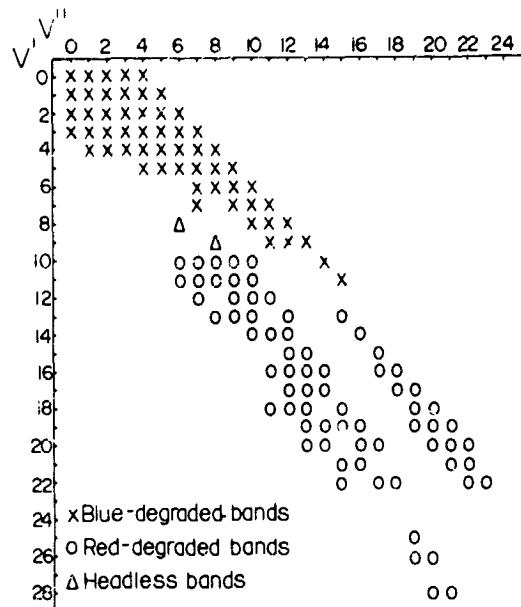


Fig. 2. Deslandres table showing the vibrational distribution and degradation of the observed bands of the N₂ first negative system.

simple. Each band consists of two branches, a *P* branch and an *R* branch and the band origin is quite apparent at low rotational temperatures. Under high resolution it can be seen that each component of each branch is a doublet. The intensity alternation of successive lines of any branch, a characteristic of the spectrum of a symmetric molecule, is also apparent. However, in some bands under certain conditions of excitation, this effect can be obscured by superposition of lines of the *P* and *R* branches with different statistical weights. Rotational perturbations have been reported in the following vibrational levels of the *B* $^2\Sigma$ state, $v = 0$ (Childs 1932); $v = 1$ (Fasbender 1924, Coster and Brons 1931); $v = 3$ (Coster and Brons 1931, Crawford and Tsai 1935); $v = 5$ (Parker 1933b), $v = 6$ (Brons 1934); $v = 13$ (Parker 1933a); $v = 14-16$, 22, 26, 27, 29 (Douglas 1952). One rotation perturbation has been reported in the *X* $^2\Sigma$ state, for the $v = 7$ level (Tyte 1963).

These perturbations affect both the intensity and position of the individual rotational lines.

3. OCCURRENCE

Sources of the Nitrogen first negative system are varied. It occurs in the negative glow of any discharge through nitrogen or through a mixture

of gases containing nitrogen. A discharge through a rare gas (particularly helium) containing a trace of nitrogen is a very good source of the system. It can also be excited in microwave discharges, hollow cathode discharges and frequently occurs in the different types of afterglows which can be excited in nitrogen. It is somewhat more difficult however to excite the system without also exciting the overlapping and very strong second positive system of nitrogen. Papers by Herzberg (1928), Parker (1933), Douglas (1952) and Janin and Eyrand (1954) all describe discharge conditions favourable for excitation of the system. It is also a prominent feature of the spectrum excited by the passage of an ion beam through nitrogen (Nicholls, Reeves and Bromley 1960, Lowe and Ferguson 1965).

The system is a major contributor to the molecular spectrum of the aurora and occurs in the twilight, day and night airglows. A complete summary of the occurrence of the system under these conditions is given by Chamberlain (1931).

4. HISTORICAL SURVEY

Though the First Negative system has been known and associated with Nitrogen since the 1880's the first worker to achieve any success in analysing it was Fasbender (1924) who made a partial rotational analysis and gave a list of 36 bandheads.

The vibrational analysis was performed by Herzberg (1928) who observed many new bands. Wood and Dieke (1938, 1940) studied the isotope effect in this system using ^{14}N - ^{15}N and ^{15}N - ^{15}N and confirmed Herzberg's vibrational analysis. Little further work on extending the vibrational analysis was done until Douglas (1952) re-examined the system in detail identifying many bands with high vibrational quantum numbers, and Janin and Eyrand (1954) observed a number of bands with intermediate vibrational quantum numbers.

The rotational analysis commenced by Fasbender (1924) was extended by Merton and Pilley (1925) and in the period 1930-35 much work was done on this by Coster and Brons (1931), Childs (1932), Parker (1933a, b), Brons (1934) and Crawford and Tsai (1935). Douglas (1952) also analysed a number of bands. Much of this work was directed towards identifying the numerous rotational perturbations which exist in the system (see section 2). These perturbations

are caused by the interaction of the A ²Π_u state with the B ²Σ_u⁺ state and until the observation of the A ²Π_u-X ²Σ_g⁺ system by Meinel in 1950* these perturbations were the only experimental evidence as to the existence of this theoretically predicted ²Π state.

The intensities of the system have been extensively reported and most of the papers on the vibrational analysis of the system contain at least eye estimates of intensity. Other papers dealing only with the intensity of the system and the variation of its intensity with conditions of excitation have been published by Smythe and Arnot (1930), Duffendack, Revans and Roy (1934), Wallace and Nicholls (1955) and Tyte (1962). Nicholls (1961) has published a table of Franck-Condon factors to high quantum numbers.

The lifetime of the v' = 0 level of the B ²Σ_u⁺ has been measured by Bennett and Dalby (1959). They found that

$$\tau_{v=0}(N_2^+ B ^2\Sigma_u^+) = 6.58 \pm 0.35 \times 10^{-8} \text{ sec.}$$

Schumaker (1963) has measured oscillator strengths of the system excited in an arc, getting good agreement with those calculated (Nicholls 1963, 1964) using Bennett and Dalby's lifetime data.

The occurrence of the system in the auroral spectrum was first recognised by Vegard in 1913 and it has been extensively used to make temperature measurements on the aurorae since the rotational structure is very favourable for this type of work.

5. MOLECULAR STRUCTURE

As in the case of N₂, the structure of the N₂⁺ ion has been extensively studied, but many fewer levels and systems of the ion are known. Four systems are definitely attributed to N₂⁺ and these involve five states, three ²Σ and two ²Π. The relative positions of these states are shown in Fig. 1.

Mulliken (1957) has theoretically predicted a large number of N₂⁺ states, both attractive and repulsive, while Lofthus (1960) has discussed the correlation between the states of N₂⁺ and possible Rydberg states of N₂.

The upper potential curve (B ²Σ_u⁺ state) is distorted and depressed by interaction between

the C ²Σ_u⁺ state and the B ²Σ_u⁺ state. The interaction between these two states of the same species is very strong and Douglas (1952) discusses its effect in detail. The interactions which cause the numerous rotational perturbations observed are the much weaker ones between individual vibrational levels of the A ²Π_u state and the B ²Σ_u⁺ state. A theoretical treatment of a ²Π-²Σ perturbation was given by Ittmann (1931).

The Klein-Dunham potentials for the X and B states are shown in Fig. 3 and are listed in Tables IX and X. See also Gilmore (1963).

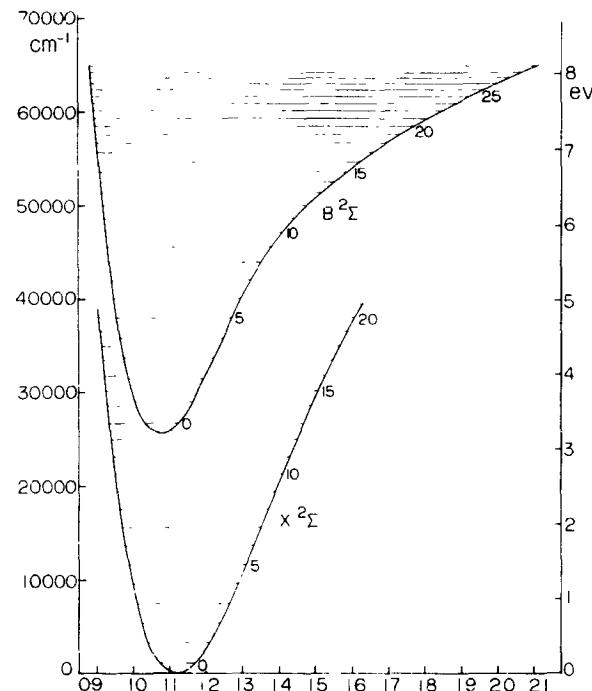


Fig. 3. Klein-Dunham potential curves for the X²Σ and B²Σ states of N₂⁺

6. MOLECULAR DATA

The fundamental constants of the X ²Σ_g⁺ and B ²Σ_u⁺ states of N₂⁺ are displayed in Table I.

The band head wavelengths (in air) and the band origin wavenumbers (*in vacuo*) are displayed in Deslandres arrays in Tables II and III respectively. For low vibrational quantum numbers the band origin wavenumbers can best be represented by the formula

$$\begin{aligned} \nu = & 25461.5 + 2419.84(v' + \frac{1}{2}) \\ & - 23.19(v' + \frac{1}{2})^2 - 0.5375(v' + \frac{1}{2})^3 \\ & - 2207.19(v'' + \frac{1}{2}) + 16.14(v'' + \frac{1}{2})^2 \\ & + 0.0400(v'' + \frac{1}{2})^3 \end{aligned}$$

*Meinel, A. B., *Astrophys. J.* **112**, 562, 1950; **114**, 431, 1951.

TABLE I
Constants of the $X^2\Sigma_g^+$ and $B^2\Sigma_u^+$ states of N_2^+

		$\mu_A = 7.00363$
$X^2\Sigma_g^+$		
T_e	= 0	
ω_e	= 2207.19 cm ⁻¹	
ω_{e,x_e}	= 16.14 cm ⁻¹	
ω_{e,y_e}	= -0.0400 cm ⁻¹	
B_e	= $2.083 - 0.0195(v + \frac{1}{2})$ cm ⁻¹	
r_e	= 1.116 Å	
$B^2\Sigma_u^+$		
T_e	= 25461.5 cm ⁻¹	
ω_e	= 2419.84 cm ⁻¹	
ω_{e,x_e}	= 23.19 cm ⁻¹	
ω_{e,y_e}	= -0.5375 cm ⁻¹	
B_e	= $1.932 - 0.020(v + \frac{1}{2})$ cm ⁻¹	
r_e	= 1.075 Å	

(1) Data and nomenclature from Herzberg (1950). The values are based on band origin measurements.

(2) Because of perturbations of the upper level it is safer in calculations involving large v to use the actual observed values for B_e and G_e rather than the derived constants. These values are given in Table IV.

(3) The ground state $X^2\Sigma_g^+$ of N_2^+ lies 125672 cm⁻¹ above the $X^1\Sigma_g^+$ ground state of the N_2 molecule.

(4) The dissociation energy of N_2^+ has been uncertain for many years. There are two possible values. The correct one is now considered to be 70398 ± 40 cm⁻¹ ($8.725 \pm .005$ eV) (Gaydon 1953).

However because of the vibrational perturbations of the upper state mentioned above, in all calculations involving large vibrational quantum numbers the observed energy levels and intervals listed in Table IV should be used rather than this formula.

Franck-Condon factors and r -centroids appropriate to the Morse potentials are displayed in Tables V and VI, but, again because of the vibrational perturbations of the $B^2\Sigma_u^+$ state, the values for high quantum numbers (say $v > 7$) should be treated with some reserve.

Table VII displays Einstein A coefficients, oscillator strengths ($f_{r,r'}$) and absolute band strengths ($S_{r,r'}$) while Table VIII compares the intensities of the main bands of the system as observed by a number of workers under a variety of excitation conditions. Tables IX and X give the numerical values of the Klein-Dunham potentials for the two states. The half integral values of $v + \frac{1}{2}$ represent real energy levels and turning points, the integral values represent interpolated, imaginary, energy levels and turning points.

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While not claiming to be complete it is hoped that most of the relevant papers are contained in this list.

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TABLE IV
Observed Vibrational Levels, Vibrational Energy Intervals and Rotational Constants

v	B $^2\Sigma_u^+$ State			X $^2\Sigma_g^+$ State		
	$T_e + G_v$ (cm ⁻¹)	ΔG_{v+1} (cm ⁻¹)	B_v (cm ⁻¹)	$T_e + G_v$ (cm ⁻¹)	ΔG_{v+1} (cm ⁻¹)	B_v (cm ⁻¹)
0	26659.7	2371.5	2.073	1099.3	2174.8	1.922
1	29031.2	2318.8	2.049	3274.1	2142.2	1.902
2	31350.0	2260.4	2.025	5416.3	2109.4	1.879
3	33610.4	2196.4	2.002	7525.7	2076.4	1.861
4	35806.8	2122.8	1.968	9602.1	2043.0	1.841
5	38729.6	2041.0	1.926	11645.1	2009.2	1.826
6	39970.6	1951.1	1.896	13654.3	1975.7	1.808
7	41921.7	1838.2	1.852	15630.0	1939.9	1.781
8	43759.9	1726.9	1.810	17569.9	1907.0	1.766
9	45486.8	1596.7		19476.9	1872.1	1.740
10	47083.5	1479.9	1.710	21349.0	1836.8	1.724
11	48563.4	1371.4	1.653	23185.8	1801.1	1.703
12	49934.8	1276.3	1.595	24986.9	1764.8	1.683
13	51211.1	1196.3	1.545	26751.7	1728.1	1.663
14	52407.4	1126.6	1.494	28479.8	1691.1	
15	53534.0	1067.1	1.452	30170.9	1653.5	1.62
16	54601.1	1015.5		31824.4	1615.4	1.593
17	55616.6	(966)		33439.8	1576.8	1.572
18	56582.6	(922)		35016.6	1537.3	
19	57504.6	(882)		36553.9	1497.7	1.522
20	58386.6	(845)		38051.6	1458.2	1.500
21	59231.6	810		39509.8		1.475
22	60041.6	775	1.188			
23	60816.6	744				
24	61560.6	717.7				
25	62278.3	690.3				
26	62968.6	661.8	1.063			
27	63630.4	637.6	1.036			
28	64268.0	607.4				
29	64875.4		0.977			

Data from Douglas (1952).

There seems to be no reliable estimate of D_v 's for the B $^2\Sigma_u^+$ state. Carroll (1959) gives 6.1×10^{-6} as an average D_v for the X $^2\Sigma_g^+$ states and some B values which differ slightly from those above and which are probably less accurate.

TABLE VI
r-Centroids (A) Appropriate to Morse Potentials

$v' \setminus v''$	0	1	2	3	4	5	6
0	1.1007	1.0529	1.0144	0.9802	0.9483	0.9173	0.8860
1	1.1529	1.1132	1.0588	1.0192	0.9848	0.9529	0.9223
2	1.2188	1.1615	1.1380	1.0650	1.0239	0.9892	0.9574
3	1.3225	1.2278	1.1709		1.0720	1.0287	0.9935
4		1.3364	1.2371	1.1814		1.0802	1.0335
5			1.3513	1.2467	1.1930		1.0908
6				1.3672	1.2567	1.2062	

Data from R. W. Nicholls, unpublished work.

TABLE II
Wavelength (A) (in air) and Wavenumbers (cm^{-1}) (*in vacuo*) of the Observed Bandheads

$v' \setminus v''$	0	1	2	3	4	5	6	7	8	9	10	11
0	3914.4	4278.1	470.2	3228.3	5864.7							
	25542.1	23368.3	21229.1	19121.4	17046.5							
1	3582.1	3884.3	4236.5	4651.8	5148.8	5754.4						
	27908.6	25739.4	23600.6	21491.1	19416.6	17373.2						
2	303.0	3563.9	3857.9	4199.1	4599.7	5076.6	5653.1					
	30221.1	28051.2	25913.5	23807.9	21734.5	19692.7	17684.5					
3	3078.2	3298.7	3548.9	3835.4	4166.8	4554.1	5012.7	5546.1				
	32489.8	30306.3	28169.7	26065.5	23992.5	21952.1	19943.8	18025.7				
4		3076.4	3293.4	3538.3	3818.1	4140.5	4515.9	4957.9	5485.5			
		32500.3	30355.0	28254.1	26183.6	24144.9	22137.8	20164.2	18224.8			
5			3291.6	3532.6	3806.8	4121.3	4490.3	4913.2	5420.8			
			30371.6	28399.7	26261.4	24257.4	22264.0	20347.7	18442.3			
6					4110.9	4466.6	4881.7	5272.3				
						24318.7	22382.1	20479.0	18961.8			
7						3808.1		4459.3	4864.4	5340		
							26252.4		22418.8	20551.8	18720	
8									4466.6	4864		
										22382.1	20551	
9					3137.0					4489		
					31868.4						22270	
10				2987.5	3174.4	3381.5	3612.6	3875.1				
				33463.1	31492.9	29564.2	27673.0	25798.5				
11				2861.7	3033.0	3222.6	3433.0	3668.1				
				34934.0	32961.1	31021.9	29120.7	27254.3				
12					2912.5		3280.0	3493.4	3733			
					34324.7		30479.1	28617.2	26779			
13						2970.0	3148.5	3345.7				
						33660.2	31752.0	29880.6				
14								3217.7	3419			
								31069.2	29234			
15									3065.1			
									32615.9			
16										3181		
										31418		
17												
18										2992		
										33409		
19												
20												
21												
22												
23												
24												
25												
26												
27												
28												
29												

This table was compiled using data from Douglas (1952), Herzberg (1928), Janin and Eyrand (1954), Merton and Pilley (1925), Stoebner, Delbourgo and Laffitte (1962, 1964), and Tyte (1963).

TABLE II—(Continued)

'\v''	12	13	14	15	16	17	18	19	20	21	22	23
0												
1												
2												
3												
4												
5												
6												
7												
8	5330.0											
	18756.5											
9	4883.3	5344.7										
	20472.3	18704.9										
10		5384.3										
		18567.4										
11	4680.0		5450.0									
		21361.6		18343.5								
12												
13	3808.9		4743.1									
	26246.9		21077.4									
14	3643.2		4850.7									
	27440.6		20610.0									
15	3500.6	3730.3		4969.3								
	28558.4	26799.9		20118.0								
16	3374.6	3588.6	3824.7		4720.2	5099.8						
	29624.7	27858.1	26138.5		21177.0	19603.2						
17	3263.0	3460.8	3682.1		4850.0	5240.2						
	30637.8	28886.8	27150.7		20612.8	19078.0						
18	3160.5	3349.6	3782.8		4988.2	5391.1						
	31631.4	29845.8	26428.0		20041.7	18543.9						
19	3250.1	3443.7	3655.7	3891.8		4769.3	5136.4	5551.9				
	30759.4	29030.2	27340.8	25687.8		20961.6	19465.0	18006.9				
20	3150.8	3341.7		3761.6	4006.7		4913.5	5292.9	5721.9			
	31638.4	29916.3		26576.9	24951.2		20346.4	18888.0	17471.9			
21		3439.2	3646.1					5066.2	5458.2			
		29068.2	27418.8					19733.2	18316.0			
22		3345.7		3756.1	3994.9				5227.7	5632.1		
		29880.6		26615.8	25024.9				19123.6	17750.5		
23		3447.3										
		29000.8										
24		3184.6										
		31392.1										
25												
26				3783.4								
				26423.8								
27				3691.5	3907.6							
				27081.6	25583.9							
28							3726.4	3940.6				
							26828.0	25369.7				

TABLE III
Wavenumbers (*in vacuo*) (cm⁻¹) of Observed Band Origins

<i>v'</i> \ <i>v''</i>	0	1	2	3	4	5	6	7	8	9	10
0	25566.0	23391.2	21249.0	19139.7							
1			23020.5	21511.3	19434.7						
2			25939.8	23830.0	21753.7	19710.4					
3					24013.9	21971.1					
4						22158.3	20182.6				
5				30427.6			22305.4	20365.5			
6								22406.5	20499.0		
7										20578.0	
8							30112.0				
9											
10						33435.2	31459.6	29518.5	27611.3		
11						34915.7	32940.1	30998.7			27119.8
12											
13											
14											31063.6
15											
16											
17											
18											
19											
20											
21											
22											
23											
24											
25											
26											
27											
28											
29											

Data collected from Crawford and Tsai (1935), Coster and Brons (1932), Douglas (1952), Parker (1933a, b), Stoebner, Delbourgo and Laffitte (1964), and Tyte (1963).

TABLE III—(Continued)

v'	v''	11	12	13	14	15	16	17	18	19	20	21
0												
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12	26754.2											
13		26229.4				21044.5						
14	29226.8		27425.7				20587.4					
15				26787.5								
16				27854.6								
17												
18												
19												
20												
21												
22						26607.0						
23												
24												
25												
26							26419.7					
27							27081.5		25583.8			
28												
29								26827.7		25369.5		

TABLE V
Franck-Condon Factor Array to Large Vibrational Quantum Numbers

$v' \setminus v''$	0	1	2	3	4	5	6	7	8	9	10
0	6.5094-1	2.5883-1	7.0162-2	1.5997-2	3.2972-3	6.3420-4	1.1549-4	1.9998-5	3.2805-6	5.0335-7	7.0274-8
1	3.0144-1	2.2260-1	2.8598-1	1.3242-1	4.2726-2	1.1403-2	2.6998-3	5.8613-4	1.1849-4	2.2393-5	3.9313-6
2	4.5371-2	4.0599-1	5.0646-2	2.2901-1	1.6535-1	7.1133-2	2.3623-2	6.6908-3	1.6951-3	3.9336-4	8.4449-5
3	2.2475-3	1.0562-1	4.1372-1	2.1005-3	1.5566-1	1.7060-1	9.4514-2	3.8008-2	1.2612-2	3.6075-3	9.6386-4
4	1.4521-5	6.9353-3	1.6604-1	3.7922-1	6.7256-3	9.2901-2	1.5692-1	1.0964-1	5.2363-2	2.0033-2	6.5985-3
5	4.6340-7	3.9858-5	1.3305-2	2.2051-1	3.3100-1	2.9248-2	4.8153-2	1.3327-1	1.1606-1	6.4883-2	2.8257-2
6	9.4819-9	3.0877-6	5.7286-5	2.0691-2	2.6731-1	2.8304-1	5.3307-2	2.0444-2	1.0647-1	1.1499-1	7.4424-2
7	6.4377-10	3.4169-8	1.1319-5	4.9298-5	2.7894-2	3.0677-1	2.4145-1	7.2364-2	5.9387-3	8.0835-2	1.0837-1
8	4.1998-13	5.7552-9	4.9506-8	3.0053-5	1.8070-5	3.4188-2	3.4009-1	2.0830-1	8.4684-2	4.7434-4	5.8649-2
9	1.2746-12	3.8766-12	2.6591-8	1.7424-8	6.4203-5	1.0666-6	3.8904-2	3.6856-1	1.8373-1	9.0654-2	5.5515-4
10	3.9487-14	1.0275-11	1.7096-10	8.3563-8	3.2950-8	1.1610-4	8.0941-5	4.1527-2	3.9326-1	1.6717-1	9.1407-2
11	2.8767-16	6.9997-13	3.8767-11	1.6762-9	1.9686-7	6.7150-7	8.230-4	3.8725-4	4.1704-2	4.1493-1	1.5792-1
12	5.2594-16	2.4906-15	5.5598-12	7.8486-11	9.1842-9	3.5933-7	3.5224-6	2.5089-4	1.0871-3	3.9276-2	4.3379-1
13	7.4212-20	9.9105-16	1.0091-13	2.7547-11	5.7016-11	3.5189-8	4.9932-7	1.1720-5	3.0102-4	2.3614-3	3.4320-1
14	1.7188-16	9.8952-17	1.3821-15	9.9713-13	9.4783-11	1.3391-11	1.0410-7	4.7645-7	3.0048-5	3.0712-4	4.3643-3
15	1.8407-16	4.0381-17	2.6642-15	3.0960-15	7.6533-12	2.2485-10	1.1384-9	2.4797-7	2.0416-7	6.3998-5	2.4992-4
16	1.8159-17	5.4575-18	2.8290-15	6.5616-15	2.0529-14	3.6688-11	3.6122-10	8.9261-9	4.8200-7	1.5601-8	1.1714-4
17	9.5257-17	1.3459-16	1.3306-15	1.5689-15	5.3219-14	1.1348-12	1.2484-10	2.8360-10	3.8957-8	7.5533-7	1.3451-6
18	3.2282-16	6.4620-16	2.7374-17	3.0826-15	7.6808-15	4.8177-14	8.8436-12	3.2815-10	2.0518-15	1.2246-7	9.0082-7
19	3.0466-16	6.7846-16	1.1417-16	2.9053-15	3.1337-17	7.9994-17	3.1504-14	4.3885-11	6.1538-10	1.8661-9	3.0166-7
20	6.8290-17	1.0853-16	4.7800-17	1.3187-16	1.9387-16	1.0090-14	1.0265-13	1.2416-12	1.6333-10	7.0155-10	1.6088-8
21	2.0273-17	6.9310-17	2.1950-17	1.2681-15	2.4681-15	7.1429-16	7.4978-14	6.1713-14	1.2370-11	4.3238-10	2.3013-1
22	1.6131-16	5.1946-16	2.1950-17	2.0731-15	1.1194-15	1.1293-15	1.8187-14	1.0151-13	8.6085-15	6.8228-11	8.3364-1
23	3.0809-16	7.5001-16	1.8879-18	5.7561-16	2.8680-16	5.7740-16	8.7811-18	5.5815-14	2.4374-13	3.2389-12	2.4321-1
24	2.6276-16	4.0819-16	2.2567-16	3.9537-17	2.8615-15	3.7123-15	2.7915-15	2.7967-14	8.7905-14	7.2159-14	3.0774-1
25	7.3746-17	7.2516-17	5.2749-16	3.2663-16	2.1827-15	1.4253-15	3.9308-16	4.4983-15	1.0689-14	2.0665-13	1.5994-1
26	2.6573-18	1.4601-17	4.5026-16	2.0016-16	5.8352-17	3.0164-16	2.0010-15	1.9009-15	5.6924-16	7.6241-15	6.6945-1
27	1.0392-16	1.4208-16	8.1945-17	6.7362-18	8.7095-16	2.7341-15	4.5872-15	1.1201-14	2.1936-15	6.4900-14	3.8017-1
28	2.6226-16	2.7250-16	3.3132-17	2.8661-17	1.9786-15	2.3088-15	8.0611-16	1.1309-14	2.8800-14	1.4500-13	4.4470-1
29	2.6659-16	3.2371-16	3.0606-16	2.8421-17	1.0866-15	1.7611-16	1.8939-15	6.6923-15	9.2761-14	9.0932-14	1.4744-1

Data from R. W. Nicholls 1961. These Franck-Condon factors are appropriate to Morse potentials and those for high quantum numbers may be not entirely reliable because of the perturbations in the $B^2\Sigma_u^+$ state.

TABLE V—(Continued)

v''	11	12	13	14	15	16	17	18	19	20	21
0	8.4194-9	7.4706-10	2.7246-11	1.5572-12	5.7438-12	4.0732-12	1.9329-12	7.4034-13	2.4709-13	6.8549-14	1.6424-14
1	6.2862-7	8.7554-8	9.5331-9	5.6580-10	2.7584-13	4.1016-11	3.8737-11	2.1156-11	9.2253-12	3.5745-12	1.2773-12
2	1.6754-5	3.0305-6	4.8313-7	6.2656-8	5.2243-9	5.9097-11	1.2927-10	1.8980-10	1.2444-10	6.0838-11	2.5444-11
3	2.3237-4	5.1559-5	1.0110-5	1.8810-6	2.8382-7	3.0499-8	1.1388-9	1.9308-10	5.9079-10	4.8728-10	2.7405-10
4	1.9422-3	5.2074-4	1.2807-4	2.8771-5	5.7951-6	9.9985-7	1.3165-7	8.8002-9	5.3633-11	1.3336-9	1.4349-9
5	1.0429-2	3.4058-3	1.0071-3	2.7242-4	6.7369-5	1.5032-5	2.9233-6	4.5566-7	4.4113-8	3.8150-10	2.0816-9
6	3.6515-2	1.4962-2	5.3781-3	1.7413-3	5.1455-4	1.3912-4	3.4114-5	7.3925-6	1.3305-6	1.6789-7	6.7916-9
7	8.0508-2	4.4113-2	1.9912-2	7.8225-3	2.7556-3	8.8413-4	2.5973-4	6.9513-5	1.6626-5	3.3928-6	5.2530-7
8	9.8214-2	8.3188-2	5.0528-2	2.4953-2	1.0647-2	4.0574-3	1.4059-3	4.4632-4	1.2057-4	3.3924-5	7.7377-6
9	4.0751-2	8.6284-2	8.2879-2	5.5439-2	2.9771-2	1.3721-2	5.6271-3	2.0953-3	7.1529-4	2.2401-4	6.3751-5
0	3.6010-3	2.7101-2	7.3930-2	8.0178-2	5.8721-2	3.4009-2	1.6889-2	7.4191-3	2.9555-3	1.0800-3	3.6310-4
1	8.8180-2	7.8956-3	1.7195-2	6.2084-2	7.5740-2	6.0410-2	3.7741-2	1.9994-2	9.3675-3	3.9758-3	1.5488-3
2	1.5540-1	8.2045-2	1.2382-2	1.0343-2	5.1312-2	7.0185-2	6.0656-2	4.0577-2	2.2892-2	1.1393-2	5.1321-3
3	4.4957-1	1.5933-1	7.3838-2	1.6506-2	5.8379-3	4.1892-2	6.4044-2	5.3684-2	4.2358-2	2.5466-2	1.3412-2
4	2.7223-2	4.6145-1	1.6967-1	6.4180-2	2.0049-2	3.0433-3	3.3901-2	5.7743-2	5.7746-2	4.3701-2	2.7626-2
5	7.1648-3	1.8762-2	4.6808-1	1.8661-1	5.3547-2	2.3010-2	1.4302-3	2.7284-2	5.1592-2	5.5097-2	4.4065-2
6	1.3548-4	1.0676-2	1.0178-2	4.6761-1	2.1044-1	4.2359-2	2.5526-2	5.8439-4	2.1907-2	4.5804-2	5.1972-2
7	1.8672-4	2.0326-5	1.1586-2	2.32073-3	4.5788-1	2.4131-1	3.1069-2	2.7824-2	1.9790-4	1.7599-2	4.0509-2
8	7.5652-6	2.5870-4	3.5495-5	1.8313-2	1.9948-5	4.3662-1	2.7903-1	2.0265-2	3.0199-2	5.4549-5	1.4183-2
9	6.8357-7	2.4387-5	3.0557-4	3.9546-4	2.1029-2	3.0089-3	4.0194-1	3.2267-1	1.0750-2	3.2999-2	1.6955-5
10	5.9409-7	1.3334-7	5.8697-5	2.9260-4	1.3714-3	2.1794-2	1.4370-2	3.5292-1	3.7021-1	3.5923-3	3.6642-2
11	6.9591-8	9.1908-7	3.4595-7	1.1445-4	1.9932-4	3.2078-3	1.9842-2	3.5454-2	2.9044-1	4.1810-1	1.2231-4
12	5.0037-10	2.0893-7	1.0338-6	4.6938-6	1.8534-4	5.9069-5	5.9731-3	1.5008-2	6.5937-2	2.1796-1	4.6109-1
13	1.0306-9	1.0520-8	4.7806-7	6.4729-7	1.9630-5	2.4734-4	8.0611-6	9.3682-3	8.2444-3	1.0298-1	1.4206-1
14	6.5049-10	3.7077-10	5.8628-8	8.4343-7	2.1043-8	5.3360-5	2.5985-4	3.1278-4	1.2586-2	2.0152-3	1.4068-1
15	1.4345-10	1.1228-9	7.4423-10	2.0164-7	1.0704-6	1.3360-6	1.1017-4	1.8749-4	1.3264-3	1.4378-2	2.1219-4
16	1.4755-11	4.0176-10	8.5840-10	1.6039-8	4.8573-7	7.4719-7	1.0525-5	1.7906-4	5.2861-5	3.3301-3	1.3483-2
17	4.5578-14	4.7793-11	6.8930-10	8.1140-12	8.0276-8	8.1718-7	3.5258-8	3.6910-5	2.2192-4	1.7120-5	6.2372-2
18	2.0445-12	6.7752-13	1.4968-10	1.0541-9	2.5762-9	2.3337-7	8.9840-7	1.3616-6	8.5564-5	1.8547-4	4.3123-4
19	6.2502-12	1.9120-11	7.1972-12	9.0426-10	1.6712-9	2.2423-8	5.1404-7	4.9309-7	1.0523-5	1.4399-4	6.6619-5

TABLE VII
Einstein A Coefficients, Oscillator Strengths ($f_{v'v''}$) and Absolute Band Strengths ($S_{v'v''}$)

$v' \setminus v''$	0	1	2	3	4
0	1.24+7	2.20+6	5.01+5	1.05+5	
	1.90-2	6.03-3	1.67-3	4.29-4	
	3.90-1	1.66-1	5.06-2	1.45-2	
1	3.42+6	2.68+6	2.66+6	1.93+6	2.74+5
	6.58-3	6.07-3	7.15-3	6.27-3	1.09-3
	1.52-1	1.52-1	1.95-1	1.88-1	3.61-2
2	8.26+5	4.79+6	7.82+5	2.32+6	1.31+5
	1.36-3	9.13-3	1.75-3	6.15-3	4.15-4
	2.89-2	2.09-1	4.34-2	1.66-1	1.23-1
3		1.88+6	5.19+6		
		3.06-3	9.80-3		
		6.50-2	2.24-1		

 $A_{v'v''} (\text{sec}^{-1})$. $f_{v'v''}$ $S_{v'v''} (a_0^2 e^2)$ (atomic units)².

Data from Nicholls (1963).

TABLE VIII
Relative Intensities of the Principal Bands of the System Excited in Various Sources

Band	Smythe and Arnot (1930)†	H.V. discharge	Electron excitation	Duffendack, Revans and Roy (1934)†	+ve ion exitn. in a He + N ₂ mixture	Electron excitation in pure N ₂	Wallace and Nicholls (1955)§	Nitrogen + Helium Mixture	Tyte (1962)§	Helium and Nitrogen Mixture
0,0	100	100	100	100	100	100	100	100	100 *	
0,1	75	80	62.5	75	45	30.5	30.5	30.5	25.3	
0,2	35	53	12.5	45	22.5	4.2	4.2	4.2	5.0	
1,0	12.5	8.6	11.4	10	10	15.1	15.1	15.1	21.0	
1,2	10	10	10	10	10	10	10	10	10 *	
1,3	5.8			6.7	4	4.3	4.3	4.3	6.0	
2,1	6.7			7.1	5	26.3	26.3	26.3	30.8	
2,4	5			5	5	5	5	5	5 *	
3,2	5			5	5				5 *	
3,4	2.9			3.0	5				0.7	
3,5	2.5			2.5	5				0.5	

*Set equal for comparison.

†Photographic intensity measurements.

§Photoelectric intensity measurements.

TABLE IX
Tabulated Klein-Dunham Potential Function, $V(r)$, X $^2\Sigma_g^+$ State of N₂⁺

$r + \frac{1}{2}$	V (cm ⁻¹)	V (ev.)	r_{min} (Å)	r_{max} (Å)
0.5	1099.6	0.136	1.072	1.166
1.0	2191.1	0.272	1.056	1.189
1.5	3274.4	0.406	1.043	1.207
2.0	4349.6	0.539	1.034	1.223
2.5	5416.6	0.671	1.025	1.237
3.0	6475.4	0.803	1.018	1.251
3.5	7526.0	0.933	1.011	1.264
4.0	8568.4	1.062	1.005	1.276
4.5	9602.4	1.190	0.999	1.288
5.0	10628.1	1.317	0.994	1.300
5.5	11645.5	1.443	0.989	1.310
6.0	12654.5	1.568	0.984	1.320
6.5	13655.0	1.692	0.979	1.331
7.0	14647.1	1.815	0.975	1.341
7.5	15630.7	1.937	0.972	1.352
8.0	16605.8	2.058	0.968	1.362
8.5	17572.2	2.178	0.964	1.372
9.0	18530.0	2.297	0.961	1.382
9.5	19479.1	2.414	0.958	1.392
10.0	20419.5	2.531	0.955	1.402
10.5	21351.1	2.646	0.952	1.411
11.0	22273.9	2.761	0.949	1.421
11.5	23187.8	2.874	0.946	1.431
12.0	24092.8	2.986	0.943	1.440
12.5	24988.8	3.097	0.940	1.450
13.0	25875.7	3.207	0.938	1.460
13.5	26753.6	3.316	0.935	1.469
14.0	27622.8	3.424	0.933	1.479
14.5	28482.4	3.530	0.931	1.489
15.0	29332.4	3.636	0.928	1.498
15.5	30172.9	3.740	0.926	1.508
16.0	31004.5	3.843	0.924	1.518
16.5	31826.5	3.945	0.922	1.528
17.0	32639.0	4.045	0.920	1.538
17.5	33441.9	4.145	0.918	1.548
18.0	34235.2	4.243	0.916	1.558
18.5	35018.7	4.340	0.915	1.568
19.0	35792.4	4.436	0.913	1.579
19.5	36556.2	4.531	0.911	1.589
20.0	37310.1	4.624	0.910	1.599
20.5	38053.9	4.716	0.908	1.610
21.0	38787.6	4.807	0.906	1.621
21.5	39511.2	4.897	0.905	1.631

TABLE X
Tabulated Klein-Dunham Potential Function, $V(r)$, $B^2\Sigma_u^+$ State of N^+

$v + \frac{1}{2}$	V (cm^{-1})	V (ev.)	r_{min} (Å)	r_{max} (Å)
0.5	1204.1	0.149	1.036	1.126
1.0	2396.0	0.297	1.020	1.147
1.5	3575.6	0.443	1.008	1.165
2.0	4742.3	0.588	0.999	1.181
2.5	5894.4	0.731	0.990	1.195
3.0	7031.9	0.872	0.983	1.209
3.5	8154.8	1.011	0.977	1.221
4.0	9262.2	1.148	0.971	1.234
4.5	10351.2	1.283	0.966	1.247
5.0	11421.8	1.416	0.961	1.259
5.5	12474.0	1.546	0.957	1.272
6.0	13505.7	1.674	0.953	1.285
6.5	14515.0	1.799	0.950	1.297
7.0	15501.8	1.921	0.946	1.310
7.5	16466.1	2.041	0.943	1.323
8.0	17395.4	2.156	0.940	1.337
8.5	18298.3	2.268	0.936	1.351
9.0	19174.9	2.377	0.934	1.365
9.5	20025.2	2.482	0.931	1.380
10.0	20838.1	2.583	0.928	1.396
10.5	21621.9	2.680	0.925	1.411
11.0	22376.5	2.773	0.923	1.428
11.5	23101.8	2.863	0.921	1.445
12.0	23799.4	2.950	0.919	1.463
12.5	24473.2	3.033	0.917	1.480
13.0	25123.2	3.114	0.916	1.498
13.5	25749.5	3.191	0.914	1.516
14.0	26356.4	3.267	0.912	1.534
14.5	26945.8	3.340	0.911	1.552
15.0	27517.8	3.411	0.909	1.571
15.5	28072.4	3.479	0.908	1.589
16.0	28612.4	3.546	0.906	1.607
16.5	29139.5	3.612	0.905	1.625
17.0	29653.7	3.675	0.904	1.643
17.5	30155.0	3.737	0.903	1.662
18.0	30643.5	3.798	0.902	1.680
18.5	31121.0	3.857	0.901	1.698
19.0	31587.5	3.915	0.900	1.717
19.5	32043.0	3.971	0.898	1.735
20.0	32488.6	4.027	0.897	1.754
20.5	32925.0	4.081	0.896	1.772
21.0	33352.1	4.134	0.895	1.790
21.5	33770.0	4.186	0.894	1.809
22.0	34179.4	4.236	0.893	1.828
22.5	34580.0	4.286	0.893	1.846
23.0	34971.9	4.334	0.892	1.865
23.5	35355.0	4.382	0.891	1.885
24.0	35730.3	4.428	0.890	1.904
24.5	36099.0	4.474	0.889	1.922
25.0	36461.1	4.519	0.888	1.941
25.5	36816.7	4.563	0.887	1.960
26.0	37165.4	4.606	0.887	1.980
26.5	37507.0	4.649	0.886	2.000
27.0	37841.5	4.690	0.886	2.019
27.5	38168.8	4.731	0.885	2.040
28.0	38491.4	4.771	0.884	2.059
28.5	38806.4	4.810	0.884	2.080
29.0	39113.9	4.848	0.883	2.101
29.5	39413.8	4.885	0.883	2.122

8. DESCRIPTION OF PLATES

It has been mentioned earlier that it is very difficult to excite the First Negative System of Nitrogen without exciting the Second Positive system also. It is possible to suppress the Second Positive system but only by using very carefully controlled conditions. Since the present work is essentially practically oriented it was felt that it would be of most use to illustrate the system under conditions in which it would normally be encountered i.e. with the Second Positive system appearing reasonably intensely.

Plate 1 shows the system under low dispersion ($\sim 60 \text{ \AA/mm}$). The source used was a hollow cathode discharge tube, passing a direct current of 200 ma through Helium containing a trace of Nitrogen at 8 mm of Hg pressure. The spectrum was taken on a Hilger f4 small quartz prism spectrograph.

Plate 2 shows the system under moderate dispersion ($\sim 15 \text{ \AA/mm}$). The source used was as for plate 1 and the spectrum was taken on a Hilger medium quartz prism spectrograph.

Plates 3 and 4 show the system under high dispersion ($\sim 5 \text{ \AA/mm}$). The source used was as for plate 1 and the spectrum was taken using the first order of a 3 metre concave grating in a Wadsworth mounting.

Plate 5 shows the system under moderate dispersion ($\sim 15 \text{ \AA/mm}$). In this spectrum the tail bands are particularly well developed. The source used was a liquid air cooled discharge of 30 ma through 200 mm Hg of Helium containing a trace (1 mm Hg) of Nitrogen and the spectrum was taken with a Hilger large quartz prism Littrow spectrograph.

Plate 6 shows the system under high dispersion ($\sim 2 \text{ \AA/mm}$). The tail bands are well developed. The source used was as for plate 5 and the spectrum was taken using the second order of a 3 m grating in an Eagle mounting.

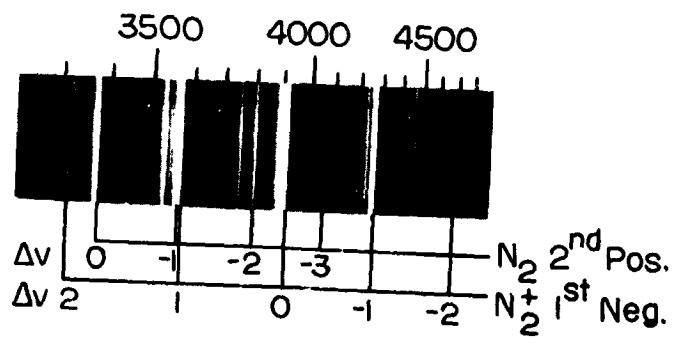


Plate I

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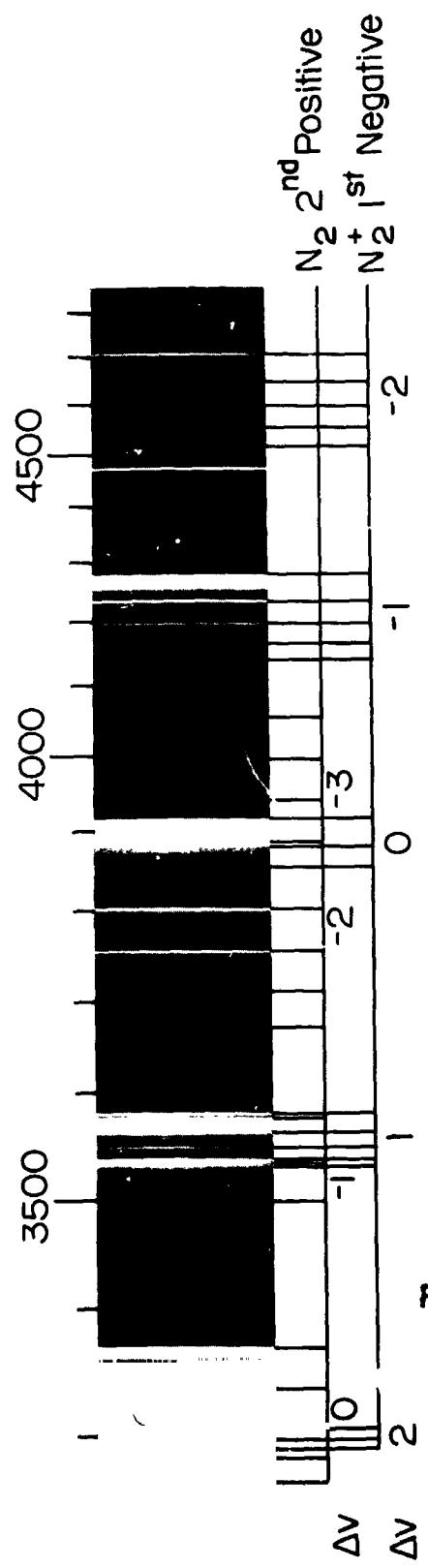
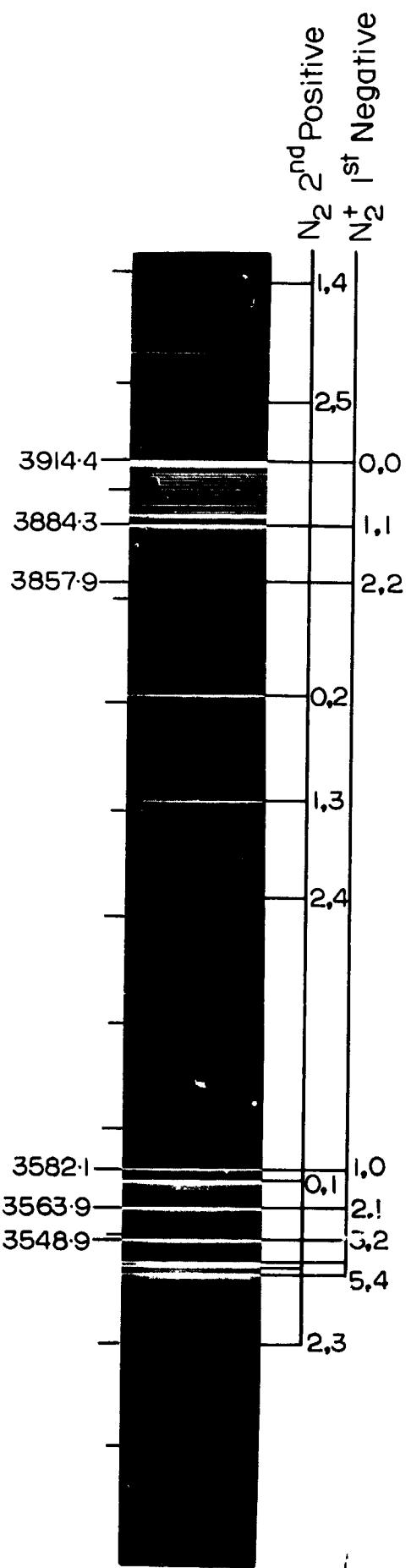
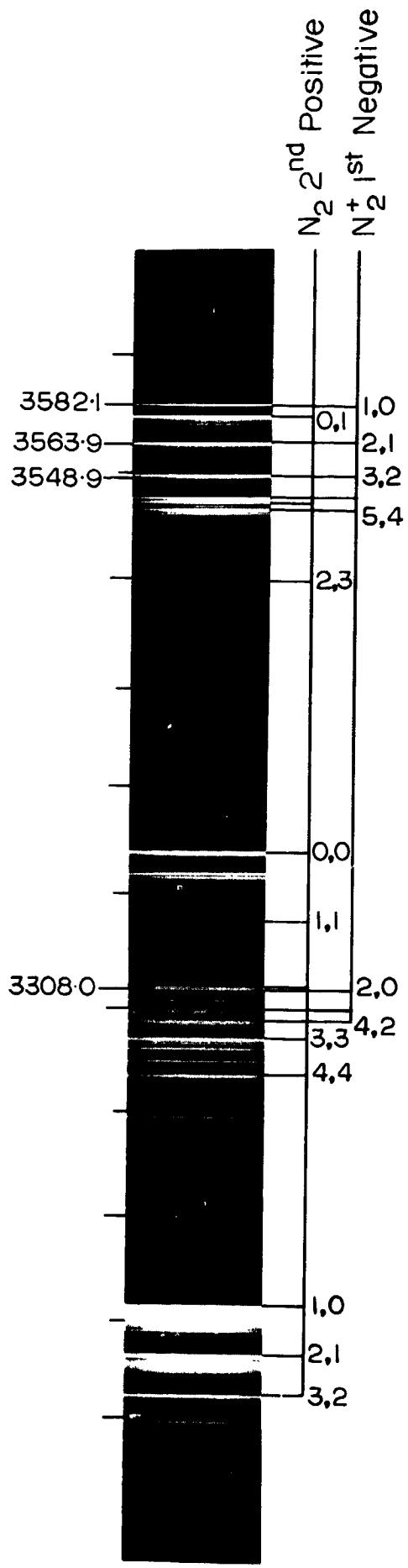


Plate 2

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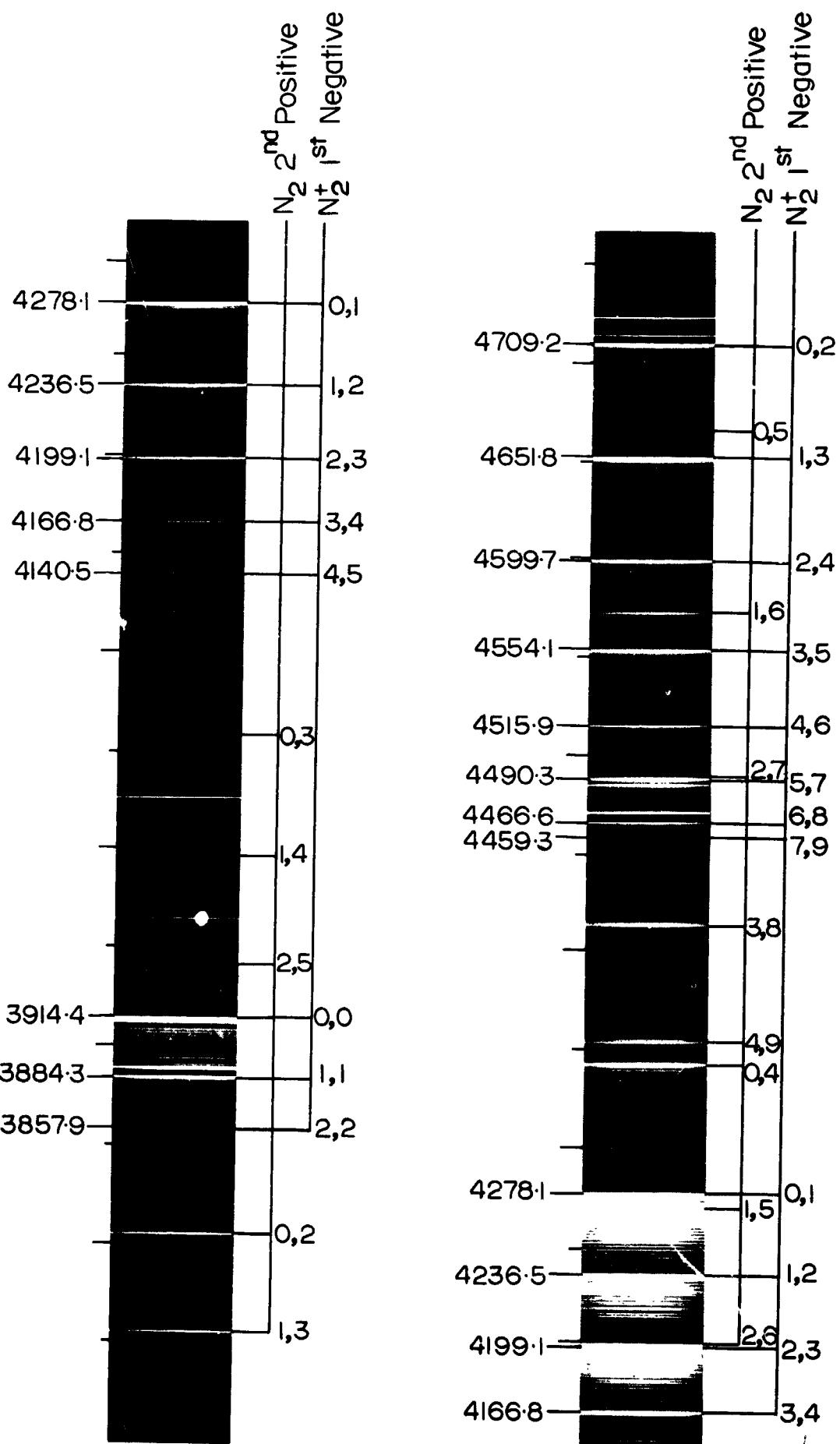


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Plate 3

PRECEDENCE, ISOTOPES AND NUCLEAR FILTERS

Plate 4



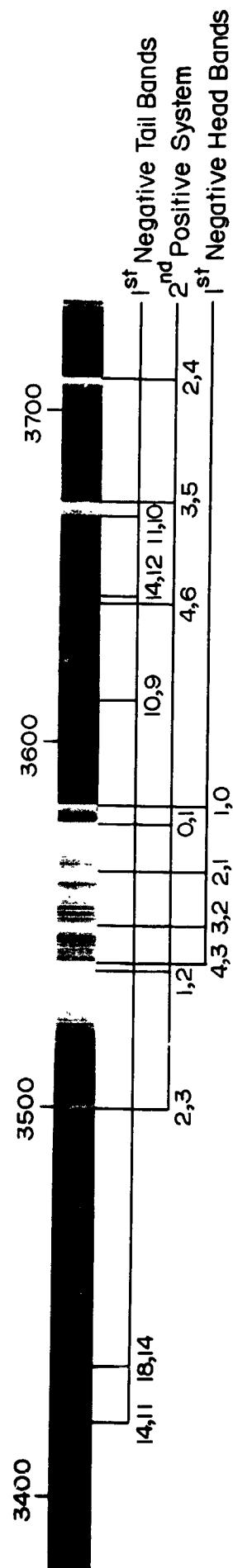
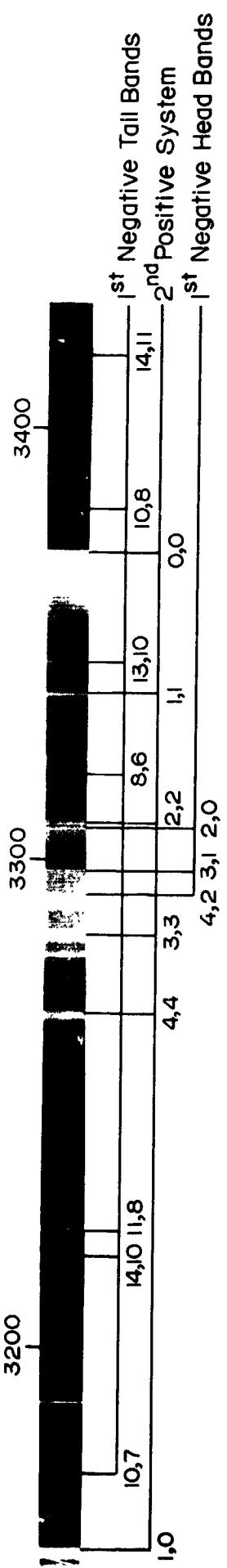


Plate 5

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